Volume 31b: Arene—X (X = N, P)

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B. Schlummer and U. Scholz

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J. L. Chiara

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J. L. Chiara

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J. L. Chiara

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A. Schmidt

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M. Begtrup and L. K. Rasmussen

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31.35 **Product Class 35: Aryl Azides**
S. Bräse, D. Keck

31.35 **Product Class 35: Aryl Azides** 1827
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31.35.1.2.1 Variation 1: From Activated Arenes 1830
31.35.1.2.2 Variation 2: By Copper-Catalyzed Reactions 1830
31.35.1.3 Method 3: Synthesis by Modification of Triazenes 1831
31.35.1.4 Method 4: Synthesis from Tetrazenes 1832
31.35.1.5 Method 5: Synthesis from Arenediazonium Salts 1832
31.35.1.6 Method 6: Synthesis from Hydrazines and Related Compounds 1834
31.35.1.7 Method 7: Synthesis from Anilines and Related Compounds 1835
31.35.1.8 Method 8: Synthesis from Nitrosoarenes 1835
31.35.1.9 Method 9: Synthesis by Rearrangement 1836
31.35.2 Applications of Product Class 35 in Organic Synthesis 1836
31.35.2.1 Method 1: Reactions with All-Carbon Functional Groups 1837
31.35.2.2 Method 2: Reactions with Heteroatom-Containing Groups 1839

31.36 **Product Class 36: Aryltriazenes, Aryltetrazenes, and Related Compounds**
S. Bräse and T. Muller

31.36 **Product Class 36: Aryltriazenes, Aryltetrazenes, and Related Compounds** 1845
31.36.1 **Product Subclass 1: Aryltetrazanes** 1846
31.36.1.1 Synthesis of Product Subclass 1 1846
31.36.1.1.1 Method 1: Dimerization of Hydrazines and Hydrazones 1846
31.36.1.1.2 Method 2: Reaction between Hydrazides and Hydrazones 1847
31.36.1.1.3 Method 3: Reaction of Azo Compounds with Hydrazones 1848
31.36.2 **Product Subclass 2: Aryltriazenes** 1849
31.36.2.1 Synthesis of Product Subclass 2 1849
31.36.2.1.1 Method 1: Synthesis from *N*-Nitrosoureas or Aryl Isocyanates 1849
31.36.2.1.2 Method 2: Synthesis from Aryl Azides 1851
31.36.2.1.3 Method 3: Synthesis from Alkyl or Acyl Azides and Arylating Agents 1853
31.36.2.1.4 Method 4: Synthesis from Arenediazonium Salts 1854
31.36.2.1.5 Method 5: Ring Opening of Cyclic Compounds 1856
31.36.2.1.6 Method 6: Modification of Triazenes by Formation of Complexes with Organometallic Reagents and Triazene Salts 1856
31.36.2.1.7 Method 7: Exchange of the Amine Functional Group in Triazenes 1858
31.36.2.1.8 Method 8: N-Alkylation of Aryltriazenes 1859
31.36.2.1.9 Method 9: N-Acylation of Aryltriazenes 1860

31.36.2.1.10 Method 10: Deacylation of Aryltriazenes 1860

31.36.3 **Product Subclass 3: Aryltriazene *N*-Oxides** 1862

31.36.3.1 Synthesis of Product Subclass 3 1862

31.36.3.1.1 Method 1: Synthesis from Diazonium Salts and Hydroxylamines 1862

31.36.3.1.2 Method 2: Synthesis from Hydrazines and Nitroso Compounds 1863

31.36.4 **Product Subclass 4: Aryltetrazenes** 1863

31.36.4.1 Synthesis of Product Subclass 4 1864

31.36.4.1.1 Method 1: Dimerization of Hydrazines 1864

31.36.4.1.2 Method 2: Modification of Tetrazenes 1865

31.36.4.1.3 Method 3: Reaction of Diazonium Salts with Hydrazines 1866

31.36.5 **Product Subclass 5: Arylpentazenes** 1867

31.36.5.1 Synthesis of Product Subclass 5 1867

31.36.5.1.1 Method 1: Reaction of Arenediazonium Salts 1867

31.36.6 **Product Subclass 6: Arylhexazenes** 1868

31.36.6.1 Synthesis of Product Subclass 6 1868

31.36.6.1.1 Method 1: Synthesis from Arenediazonium Salts and Hydrazines 1868

31.36.6.1.2 Method 2: Synthesis from 1,3-Diaryltriazenes 1869

31.37 **Product Class 37: *N*-Phosphinoarylamines**
M. Alajarín, C. López-Leonardo, and J. Berná

31.37 **Product Class 37: *N*-Phosphinoarylamines** 1873

31.37.1 **Product Subclass 1: *N*-Monophosphinoarylamines** 1873

31.37.1.1 Synthesis of Product Subclass 1 1873

31.37.1.1.1 Method 1: Aminolysis of Chlorophosphines 1873

31.37.1.1.1.1 Variation 1: Stepwise Using Dichlorophosphines 1877

31.37.1.1.1.2 Variation 2: Using Silylamines 1877

31.37.1.1.2 Method 2: Amino Interchange 1878

31.37.1.1.3 Methods 3: Miscellaneous Syntheses 1878

31.37.2 **Product Subclass 2: *N*,*N*-Diphosphinoarylamines** 1879

31.37.2.1 Synthesis of Product Subclass 2 1879

31.37.2.1.1 Method 1: Aminolysis of Chlorodiphenylphosphine 1879

31.37.2.1.2 Method 2: Synthesis Using Alkali Metal *N*-Phosphinoarylamides 1880

31.37.3 **Product Subclass 3: Bis(arylamino)phosphines** 1881

31.37.3.1 Synthesis of Product Subclass 3 1881

31.37.3.1.1 Method 1: Aminolysis of Dichlorophosphines 1881

31.37.3.1.2 Method 2: Amino Interchange 1882

31.38 **Product Class 38: Cyclic Arylamines**
P. J. Stevenson

31.38 **Product Class 38: Cyclic Arylamines** 1885
31.38.1 **Product Subclass 1: Cyclic Monoarylamines** 1886
31.38.1.1 Synthesis of Product Subclass 1 1886
31.38.1.1.1 Method 1: Formation of One C(sp^3)—N and Two C—C Bonds 1886
31.38.1.1.1.1 Variation 1: Condensation of Two Aldehydes with an Arylamine 1886
31.38.1.1.1.2 Variation 2: Condensation between an Aldehyde and an Arylamine in the Presence of 1*H*-Benzotriazole 1886
31.38.1.1.1.3 Variation 3: Reaction of an Arylamine with Two Equivalents of a Masked Aldehyde 1887
31.38.1.1.1.4 Variation 4: Intermolecular Condensation of an Arylamine, an Aldehyde, and an Alkene 1888
31.38.1.1.1.5 Variation 5: Intramolecular Condensations between Anilines and Hex-5-enals 1889
31.38.1.1.2 Method 2: Formation of One C(sp^3)—N and One C—C Bond 1890
31.38.1.1.2.1 Variation 1: 1-Alkyl-3-(trifluoromethyl)-2,3-dihydro-1*H*-indol-3-ols by Reactions of Alkoxyoxiranes with *N*-Alkylanilines 1890
31.38.1.1.2.2 Variation 2: Tetrahydroquinolines by the Cycloaddition of *ortho*-Azaxylylenes 1891
31.38.1.1.2.3 Variation 3: Tetrahydroquinolines by the Annulation of 2-Iodoanilines 1892
31.38.1.1.3 Method 3: Formation of Two C—C Bonds 1893
31.38.1.1.3.1 Variation 1: Intramolecular Diels–Alder Reactions of Furan-2-amines and Diazin-2-amines 1893
31.38.1.1.3.2 Variation 2: Intermolecular Diels–Alder Reactions between Imines and Alkenes 1894
31.38.1.1.3.3 Variation 3: Diels–Alder Reactions of *N*,*N*-, *O*,*N*-, or *S*,*N*-Acetals Derived from Arylamines with Alkenes 1895
31.38.1.1.3.4 Variation 4: Reactions of Nitrones with Electron-Deficient Allenes 1896
31.38.1.1.4 Method 4: Noncatalytic Ring Closure via Formation of a C(sp^2)—N Bond 1897
31.38.1.1.4.1 Variation 1: Benzyl-2,3-dihydro-1*H*-indoles by Aryl Radical Cyclizations onto Imines 1897
31.38.1.1.4.2 Variation 2: Reactions of Aryllithiums with Electrophilic Nitrogen Compounds 1897
31.38.1.1.4.3 Variation 3: Intramolecular Nucleophilic Aromatic Substitution Reactions 1898
31.38.1.1.5 Method 5: Catalytic Ring Closure via the Formation of a C(sp^2)—N Bond 1899
31.38.1.1.5.1 Variation 1: Palladium-Catalyzed N-Arylation Reactions 1900
31.38.1.1.5.2 Variation 2: Copper-Catalyzed Intramolecular N-Arylation Reactions 1901
31.38.1.1.5.3 Variation 3: Nickel-Catalyzed Intramolecular N-Arylation Reactions 1902
31.38.1.1.6 Method 6: Ring Closure via the Formation of a C(sp^3)—N Bond 1903
31.38.1.1.6.1 Variation 1: Carboamination of Alkenes 1903
31.38.1.1.6.2 Variation 2: Tandem Reduction of a Nitro Group and Cyclization of the Resulting Amine 1904
31.38.1.1.6.3 Variation 3: Intramolecular N-Alkylation with Acetamides or Tosylamides 1906
31.38.1.1.6.4 Variation 4: Intramolecular N-Alkylation of Alcohols 1907
31.38.1.1.6.5 Variation 5: Intramolecular N-Alkylation of Epoxides 1907

31.38.1.1.7	Method 7:	Ring Closure via the Formation of a C(sp^2)—C(sp^2) Bond	1908
31.38.1.1.7.1	Variation 1:	Synthesis by Alkene Metathesis	1908
31.38.1.1.7.2	Variation 2:	Electrophilic Acylation	1909
31.38.1.1.7.3	Variation 3:	Synthesis by the Intramolecular Electrophilic Substitution of Propargyl Trimethylsilyl Ethers	1909
31.38.1.1.7.4	Variation 4:	Intramolecular Heck Reactions	1910
31.38.1.1.8	Method 8:	Ring Closure via the Formation of a C(sp^3)—C(sp^3) Bond	1911
31.38.1.1.8.1	Variation 1:	Cyclization of Imines	1911
31.38.1.1.9	Method 9:	Ring Closure via the Formation of a C(sp^2)—C(sp^3) Bond	1912
31.38.1.1.9.1	Variation 1:	Dieckmann Cyclization of Diesters	1912
31.38.1.1.9.2	Variation 2:	Intramolecular Electrophilic Substitution	1913
31.38.1.1.9.3	Variation 3:	Radical Cyclization	1913
31.38.1.1.9.4	Variation 4:	Palladium-Catalyzed Cyclizations of *N*-Allyl-2-iodoanilines	1915
31.38.1.1.9.5	Variation 5:	Cyclization of *N*,*N*-Diallyl-2-bromoanilines	1917
31.38.1.1.9.6	Variation 6:	Zirconium-Mediated Cyclizations Involving Arynes	1918
31.38.1.1.10	Method 10:	Synthesis by Ring Transformation	1919
31.38.1.1.10.1	Variation 1:	Migration to an Electron-Deficient Nitrogen Center	1919
31.38.1.1.11	Method 11:	Synthesis by Substituent Modification	1920
31.38.1.1.11.1	Variation 1:	Asymmetric Lithiation Followed by Trapping with Electrophiles	1920
31.38.1.1.11.2	Variation 2:	Electrophilic Substitution	1921
31.38.1.1.12	Method 12:	Synthesis from Other Aromatic Heterocycles	1921
31.38.1.1.12.1	Variation 1:	Reduction of Aromatic Heterocycles	1922
31.38.1.1.12.2	Variation 2:	Oxidative Cleavage of C—C Bonds	1923
31.38.2	**Product Subclass 2: Cyclic Diarylamines**		1924
31.38.2.1	Synthesis of Product Subclass 2		1924
31.38.2.1.1	Method 1:	Formation of Two C(sp^2)—C(sp^3) Bonds	1924
31.38.2.1.2	Method 2:	Formation of One C(sp^2)—N Bond	1924
31.38.2.1.3	Method 3:	Formation of One C(sp^2)—C(sp^2) Bond	1925
31.38.2.1.4	Method 4:	Formation of One C(sp^2)—C(sp^3) Bond	1925
31.38.2.1.5	Method 5:	Synthesis from Aromatic Heterocycles	1926
31.38.2.1.5.1	Variation 1:	Reactions of Acridines with Nucleophiles	1926
31.38.2.1.5.2	Variation 2:	Reduction of Acridines	1927
31.38.3	**Product Subclass 3: Cyclic Arenediamines**		1927
31.38.3.1	Synthesis of Product Subclass 3		1927
31.38.3.1.1	Method 1:	Formation of Two C(sp^2)—N(sp^3) Bonds	1927
31.38.3.1.2	Method 2:	Formation of Two C(sp^3)—N(sp^3) Bonds	1928
31.38.3.1.2.1	Variation 1:	Reactions of Aromatic Diamines with Ketones	1928
31.38.3.1.2.2	Variation 2:	1,2,3,4-Tetrahydroquinoxalines by Reactions of Benzene-1,2-diamine with (*Z*)-But-2-ene-1,4-diol or Its Derivatives	1928
31.38.3.1.2.3	Variation 3:	Annulations with Oxirane-2-carbonitriles	1929
31.38.3.1.2.4	Variation 4:	Annulation with α,ω-Dibromoalkanes	1929
31.38.4	**Product Subclass 4: 5,10-Dihydrophenazines**		1930
31.38.4.1	Synthesis of Product Subclass 4		1930
31.38.4.1.1	Method 1:	Formation of Two C(sp^2)—N(sp^3) Bonds	1930

31.39 Product Class 39: Arylphosphonic Acids and Derivatives
I. B. Gorrell and T. P. Kee

31.39 Product Class 39: Arylphosphonic Acids and Derivatives 1939
31.39.1 Synthesis of Product Class 39 1939
31.39.1.1 Synthesis via P—C Bond Formation 1939
31.39.1.1.1 Method 1: Reactions of Nucleophilic Phosphorus 1939
31.39.1.1.1.1 Variation 1: The Arbuzov Reaction and Related Reactions 1939
31.39.1.1.1.2 Variation 2: Synthesis from Diazonium Salts 1944
31.39.1.1.2 Method 2: Reactions of Electrophilic Phosphorus 1946
31.39.1.1.2.1 Variation 1: Reactions of Phosphorus(V) Compounds with Organometallic Reagents 1946
31.39.1.1.2.2 Variation 2: Reactions of Phosphorus(III) Compounds with Organometallic Reagents 1949
31.39.1.1.2.3 Variation 3: Preparation via a Modified Friedel–Crafts Procedure 1951
31.39.1.1.2.4 Variation 4: The Phospho-Fries Rearrangement 1953
31.39.1.1.2.5 Variation 5: Direct Phosphonation of Arenes with Phosphorus Pentoxide or Pentasulfide 1956
31.39.1.1.3 Method 3: Synthesis via Free-Radical Phosphonation 1958
31.39.1.2 Synthesis via Modification of a Preformed P—C Bond Containing Framework 1958
31.39.1.2.1 Method 1: Synthesis via Transformations of Existing Arylphosphonic Acids 1958
31.39.1.2.2 Method 2: Oxidation of Arylphosphinic Acids 1960

31.40 Product Class 40: Arylphosphinic Acids and Derivatives
H.-J. Cristau and D. Virieux

31.40 Product Class 40: Arylphosphinic Acids and Derivatives 1963
31.40.1 **Product Subclass 1: Arylphosphinic Acids and Derivatives with a P═O Bond** 1963
31.40.1.1 Synthesis of Product Subclass 1 1963
31.40.1.1.1 Method 1: Arylphosphinic Halides from Trivalent Arylphosphorus Halides 1963
31.40.1.1.1.1 Variation 1: Oxidation of Aryl(monochloro)phosphines 1963
31.40.1.1.1.2 Variation 2: Alkylation of Aryldichlorophosphines 1964
31.40.1.1.1.3 Variation 3: Addition of Aryldichlorophosphines to Activated C═C Bonds 1965
31.40.1.1.1.4 Variation 4: α-Functional Alkylation of Aryldichlorophosphines 1966
31.40.1.1.2 Method 2: Arylphosphinic Halides from Tetracoordinated Phosphorus Acids and Their Derivatives 1968
31.40.1.1.2.1 Variation 1: Arylphosphinic Halides from Phosphonic Dihalides 1968
31.40.1.1.2.2 Variation 2: Arylphosphinic Halides from Phosphinic Acids and Esters ... 1969
31.40.1.1.2.3 Variation 3: Arylphosphinic Halides from Hydrogenophosphine Oxides . 1970
31.40.1.1.3 Method 3: Arylphosphinic Halides from Pentacoordinated Phosphorus Compounds 1972
31.40.1.1.4 Method 4: Arylphosphinic Acids from Phosphorus(III) Derivatives 1973

31.40.1.1.4.1	Variation 1:	Arylphosphinic Acids from Phosphorus(III) Halides by Reaction with Arenediazonium Salts	1973
31.40.1.1.4.2	Variation 2:	Arylphosphinic Acids from Phosphorus(III) Halides by Reaction with Organometallic Compounds	1974
31.40.1.1.4.3	Variation 3:	Arylphosphinic Acids from Phosphorus(III) Halides by α-Aminoalkylation	1975
31.40.1.1.5	Method 5:	Arylphosphinic Acids from Tetracoordinated Phosphorus Derivatives	1978
31.40.1.1.5.1	Variation 1:	Arylphosphinic Acids from Tetracoordinated Phosphorus Halides	1978
31.40.1.1.5.2	Variation 2:	Arylphosphinic Acids from Tetracoordinated Phosphorus Acids or Their Derivatives	1978
31.40.1.1.5.3	Variation 3:	Arylphosphinic Acids from Phosphine Oxides	1980
31.40.1.1.6	Method 6:	Arylphosphinic Esters from Phosphorus(III) Derivatives	1981
31.40.1.1.6.1	Variation 1:	Arylphosphinic Esters from Aryldichlorophosphines by Reactions with Enolizable Ketones	1981
31.40.1.1.6.2	Variation 2:	Arylphosphinic Esters from Phosphorus(III) Esters by Arbuzov Reaction or Rearrangement	1984
31.40.1.1.6.3	Variation 3:	Arylphosphinic Esters from Phosphines and Polyphosphines	1987
31.40.1.1.7	Method 7:	Arylphosphinic Esters from Tetracoordinated Phosphorus Derivatives	1987
31.40.1.1.7.1	Variation 1:	Arylphosphinic Esters from Tetracoordinated Phosphorus Halides by Reaction with Organometallic Compounds	1987
31.40.1.1.7.2	Variation 2:	Arylphosphinic Esters by α-Hydroxyalkylation of Aryl(hydrogeno)phosphinates	1988
31.40.1.1.7.3	Variation 3:	α-Aminoalkylation of Aryl(hydrogeno)phosphonates	1991
31.40.1.1.7.4	Variation 4:	Arylphosphinic Esters by Reaction of Hydrogenophosphinates with Alkenes	1993
31.40.1.1.7.5	Variation 5:	Arylphosphinic Esters by Alkylation of Hydrogenophosphinic Esters	1995
31.40.1.1.7.6	Variation 6:	Arylphosphinic Esters or Acids by Arylation of Hydrogenophosphinates	1995
31.40.1.1.7.7	Variation 7:	Arylphosphinic Esters by Hydrophosphination of Alkynes	1998
31.40.1.1.8	Method 8:	Arylphosphinic Esters from Phosphinic Acids	1998
31.40.1.1.9	Method 9:	Symmetrical Arylphosphinic Anhydrides from Tetracoordinated Phosphorus Acids and Their Derivatives	2000
31.40.1.1.9.1	Variation 1:	Symmetrical Arylphosphinic Anhydrides from Diarylphosphine Dioxides	2000
31.40.1.1.9.2	Variation 2:	Symmetrical Arylphosphinic Anhydrides from Arylphosphinic Acids and Their Derivatives	2000
31.40.1.1.10	Method 10:	Mixed Arylphosphinic–Carboxylic Anhydrides from Phosphinic Acids and Their Derivatives	2001
31.40.1.1.10.1	Variation 1:	Mixed Arylphosphinic–Carboxylic Anhydrides by Oxidation of Arylphosphinous–Carboxylic Anhydrides	2001
31.40.1.1.10.2	Variation 2:	Mixed Arylphosphinic–Carboxylic Anhydrides from Phosphinic Acids and Their Derivatives	2001
31.40.1.1.11	Method 11:	Synthesis of Arylphosphinothioic *S*-Esters	2002

31.40.1.1.11.1 Variation 1: Synthesis of Arylphosphinothioic *S*-Esters from Hydrogenophosphine Oxides 2002
31.40.1.1.11.2 Variation 2: Synthesis of Arylphosphinothioic *S*-Esters from Arylphosphinic Chlorides 2003
31.40.1.1.12 Method 12: *P*-Arylphosphinic Amides and Their Analogues from Phosphorus(III) Derivatives 2003
31.40.1.1.12.1 Variation 1: *N*-Alkylidene-*P*-arylphosphinic Amides from Diaryl(chloro)phosphines and Oximes 2003
31.40.1.1.12.2 Variation 2: *P*-Arylphosphinic Amides by Reaction of Electrophiles with Dichlorophosphines 2005
31.40.1.1.12.3 Variation 3: *P*-Arylphosphinic Amides by Reactions of Aminophosphonites 2006
31.40.1.1.12.4 Variation 4: *P*-Arylphosphinic Amides by Oxidation of Aminophosphines 2007
31.40.1.1.13 Method 13: *P*-Arylphosphinic Amides and Their Analogues from Tetracoordinated Phosphorus Derivatives 2008
31.40.1.1.13.1 Variation 1: *P*-Arylphosphinic Amides and Their Analogues from Phosphinic Chlorides 2008
31.40.1.1.13.2 Variation 2: *P*-Arylphosphinic Amides from Phosphonamidic Chlorides 2009
31.40.1.1.14 Method 14: *P*-Arylphosphinic Amides from Pentacoordinated Phosphorus Derivatives 2009

31.40.2 **Product Subclass 2: Arylphosphinothioic and Arylphosphinoselenoic *O*-Acids and Derivatives** 2010
31.40.2.1 Synthesis of Product Subclass 2 2010
31.40.2.1.1 Method 1: Arylphosphinothioic and Arylphosphinoselenoic Halides from Phosphorus Precursors without a Sulfur or Selenium Atom 2010
31.40.2.1.1.1 Variation 1: Arylphosphinothioic or Arylphosphinoselenoic Halides by Sulfuration or Selenation of Tricoordinated Phosphorus Chlorides 2010
31.40.2.1.1.2 Variation 2: Arylphosphinothioic Halides by a One-Pot Arylation–Sulfuration Reaction 2011
31.40.2.1.1.3 Variation 3: Arylphosphinothioic Halides by Thioallylation–Allylic Rearrangement 2011
31.40.2.1.1.4 Variation 4: Arylphosphinoselenoic Halides by a One-Pot Selenation–Grignard Reaction from Tricoordinated Phosphorus Compounds 2011
31.40.2.1.1.5 Variation 5: Arylphosphinothioic Halides by Sulfuration of Tetracoordinated Phosphorus Compounds 2012
31.40.2.1.2 Method 2: Arylphosphinothioic or Arylphosphinoselenoic Halides from Phosphorus Precursors Containing a Sulfur or Selenium Atom 2013
31.40.2.1.2.1 Variation 1: Halogenation of Tetracoordinated Phosphinothioic or Phosphinoselenoic Derivatives 2013
31.40.2.1.2.2 Variation 2: Oxidation of Hydrogenophosphine Sulfides 2014
31.40.2.1.2.3 Variation 3: Oxidation of Diphosphine Disulfides 2014
31.40.2.1.3 Method 3: Arylphosphinothioic *O*-Acids from Phosphorus Precursors Lacking Sulfur Atoms 2015

31.40.2.1.4 Method 4: Arylphosphinothioic or Arylphosphinoselenoic *O*-Acids from Phosphorus Precursors Containing a Sulfur or Selenium Atom 2016
31.40.2.1.5 Method 5: Arylphosphinothioic or Arylphosphinoselenoic *O*-Esters from Phosphorus Precursors Lacking a Sulfur or Selenium Atom 2016
31.40.2.1.5.1 Variation 1: Sulfuration or Selenation of Tricoordinated Phosphorus Compounds 2016
31.40.2.1.5.2 Variation 2: Sulfuration or Selenation of Tetracoordinated Phosphorus Compounds 2018
31.40.2.1.5.3 Variation 3: Sulfuration of Dicoordinated Phosphorus Compounds 2019
31.40.2.1.6 Method 6: Arylphosphinothioic or Arylphosphinoselenoic *O*-Acids or *O*-Esters from Phosphorus Precursors with a Sulfur or Selenium Atom 2019
31.40.2.1.6.1 Variation 1: Synthesis from Arylphosphinothioic or Arylphosphinoselenoic Chlorides 2019
31.40.2.1.6.2 Variation 2: Synthesis of Phosphinothioic *O*-Esters by Activation of Acids 2020
31.40.2.1.6.3 Variation 3: Reaction of Hydrogenophosphinothioates 2021
31.40.2.1.6.4 Variation 4: Ring Opening of Cyclic Derivatives 2021
31.40.2.1.6.5 Variation 5: α-Alkylation of Phosphinothioates 2022
31.40.2.1.6.6 Variation 6: Other Methods Involving Rearrangements 2022

31.41 **Product Class 41: Arylphosphine Oxides**
C. A. Ramsden

31.41 **Product Class 41: Arylphosphine Oxides** 2035
31.41.1 **Product Subclass 1: Symmetrical and Racemic Arylphosphine Oxides** 2035
31.41.1.1 Synthesis of Product Subclass 1 2035
31.41.1.1.1 Method 1: Synthesis from Phosphoryl Chloride 2035
31.41.1.1.2 Method 2: Synthesis from Phosphonic Acid Esters 2036
31.41.1.1.2.1 Variation 1: By Reaction with Organometallic Reagents 2036
31.41.1.1.2.2 Variation 2: By Rearrangement 2037
31.41.1.1.3 Method 3: Synthesis from Phosphinic Chlorides 2037
31.41.1.1.4 Method 4: Synthesis from Phosphinic Acid Esters 2038
31.41.1.1.4.1 Variation 1: By Reaction with Organometallic Reagents 2038
31.41.1.1.4.2 Variation 2: By Rearrangement 2040
31.41.1.1.5 Method 5: Synthesis from Halophosphines (Phosphinous Halides) 2040
31.41.1.1.6 Method 6: Synthesis from Phosphinous Acids and Esters 2041
31.41.1.1.6.1 Variation 1: Michaelis–Arbuzov Reaction of Alkyl Phosphinites 2041
31.41.1.1.6.2 Variation 2: By Alkylation of Phosphinite Anions 2042
31.41.1.1.6.3 Variation 3: By Metal-Catalyzed Coupling Reactions 2043
31.41.1.1.6.4 Variation 4: By 1,2-Hydrophosphination of Unsaturated Compounds 2044
31.41.1.1.6.5 Variation 5: By Rearrangement of Allyl Phosphinites 2045
31.41.1.1.7 Method 7: Synthesis from Phosphonium Salts 2046
31.41.1.1.8 Method 8: Synthesis from Phosphines 2047
31.41.2 **Product Subclass 2: Optically Active Arylphosphine Oxides** 2048
31.41.2.1 Synthesis of Product Subclass 2 2049

31.41.2.1.1 Method 1: Nucleophilic Displacement at Phosphorus 2049
31.41.2.1.2 Method 2: Alkylation at Phosphorus 2050
31.41.2.1.3 Method 3: Optical Resolution 2050
31.41.2.1.4 Method 4: Kinetic Resolution 2053

31.42 **Product Class 42: Arylphosphines and Derivatives**
P. J. Murphy and H. Böckemeier

31.42 **Product Class 42: Arylphosphines and Derivatives** 2057
31.42.1 Synthesis of Product Class 42 2057
31.42.1.1 Method 1: Electrochemical Synthesis 2057
31.42.1.2 Method 2: Nickel-Catalyzed Coupling of Arylphosphines and Aryl Trifluoromethanesulfonates 2059
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